Supporting information for

Potentiometric Response from Ion-Selective Nanospheres with Voltage-Sensitive Dyes

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Experimental Section

Reagents. Pluronic® F-127 (F127), bis(2-ethylhexyl) sebacate (DOS), Ca^{2+} ionophore IV, tetrahydrofuran (THF), methanol, ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA), potassium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB), merocyanine 540 (M540), 3,3'-dibutylthiacarbocyanine iodide (VSDA), 3,3'-diethyloxadicarbocyanine iodide (VSDB), 3,3'-dihexyloxacarbocyanine iodide (VSDC) and 1,1′-dioctadecyl-3,3,3′,3′-tetramethylindocarbocyanine perchlorate (DIL) were obtained from Sigma-Aldrich. All solutions were prepared by dissolving appropriate salts into deionized water (Mili-Q). All salts used were analytical grade or better.

Nanosphere preparation. The Ca^{2+}-selective nanospheres were prepared by dissolving 0.3 mg of NaTFPB, 0.008 mg of VSDs, 8 mg of DOS, 4.5 mg of F127, and 1.2 mg of calcium ionophore IV in 3.0 mL of methanol to form a homogeneous solution. 0.2 mL of this solution was pipetted and injected into 4.5 mL of deionized water on a vortex with a spinning speed of 1000 r/min. The resulting clear mixture was blown with compressed air on the surface for 20 min to remove methanol, giving a clear particle suspension. The K^{+}-sensitive nanospheres were prepared with the same procedure from a methanol (3 mL) cocktail containing 0.5 mg of KTFPB, 0.01 mg of VSDs, 8.0 mg of DOS, 4.5 mg of F127, and 2 mg of valinomycin.

Instrumentation and Measurement. The size of the nanospheres was measured with the particle size analyzer Zetasizer Nano ZS (Malvern Inc.). Fluorescence responses of the nanospheres were measured with a fluorescence spectrometer (Fluorolog3, Horiba Jobin Yvon) using disposable poly(methyl methacrylate) cuvettes with path length of 1 cm as sample container. Excitation wavelength was chosen as follows: 510 nm (M540), 550 nm (VSDA), 550 nm (VSDB), 460 nm (VSDC) and 520 nm (DIL). Desired analyte concentration in the nanosphere suspension was achieved by addition of calculated mount of stock solutions or solid. To characterize the response time (Fig. 2a), excitation wavelength was fixed at 550 nm while the emission at 580 nm was recorded overtime. The microscopic images (Fig. 2d) were obtained on an inverted fluorescence microscope (ECLIPSE Ti-E, Nikon) through a standard Texas Red filter cube (excitation 542 nm – 582 nm, emission: 604 nm – 644 nm).

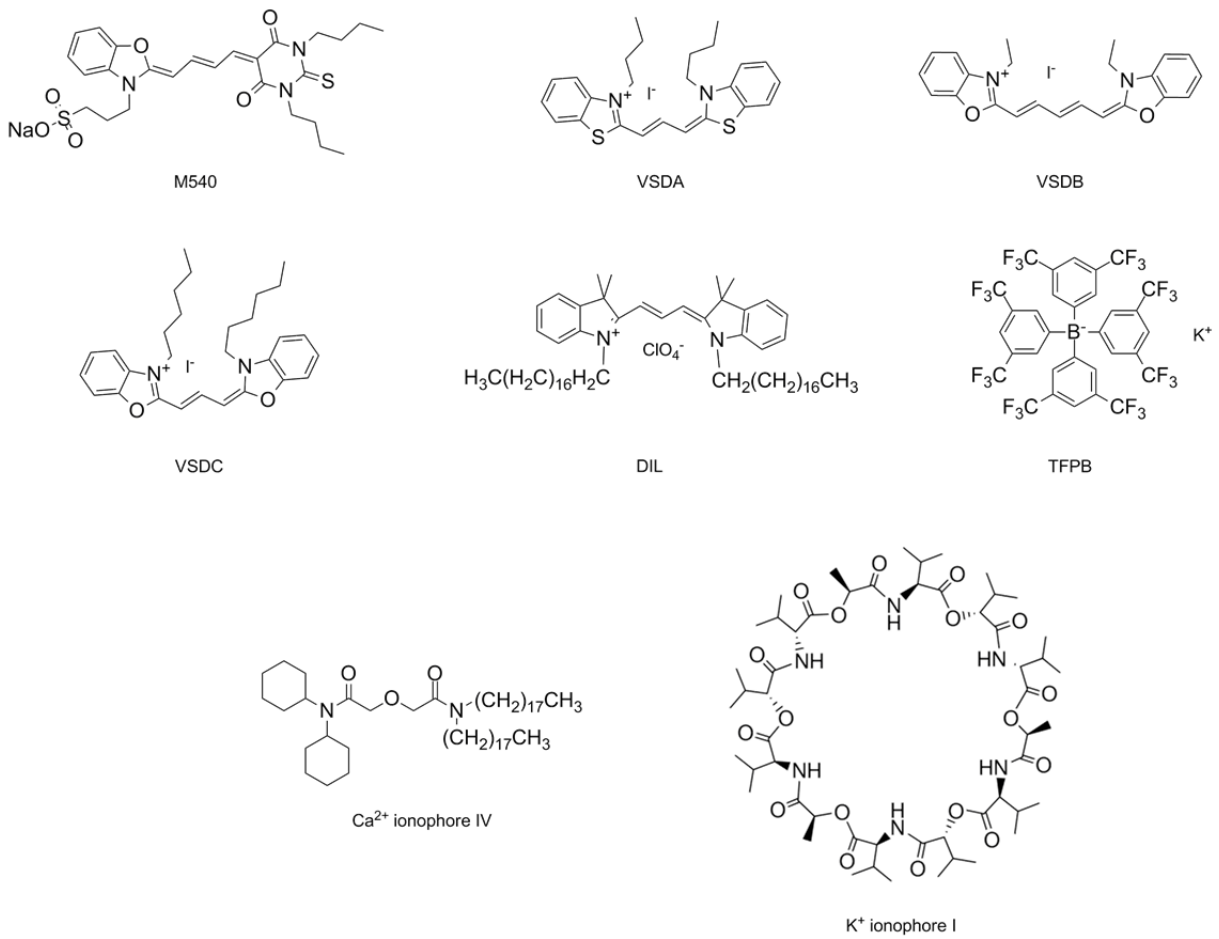

Figure S1. Chemical structures and abbreviations of VSDs, ionophores and ion exchanger used in this work.

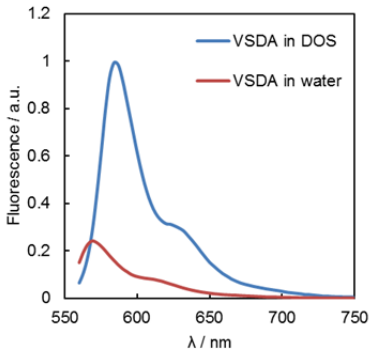

Figure S2. Fluorescence spectra of 10 μM of VSDA in H_2O and in DOS.

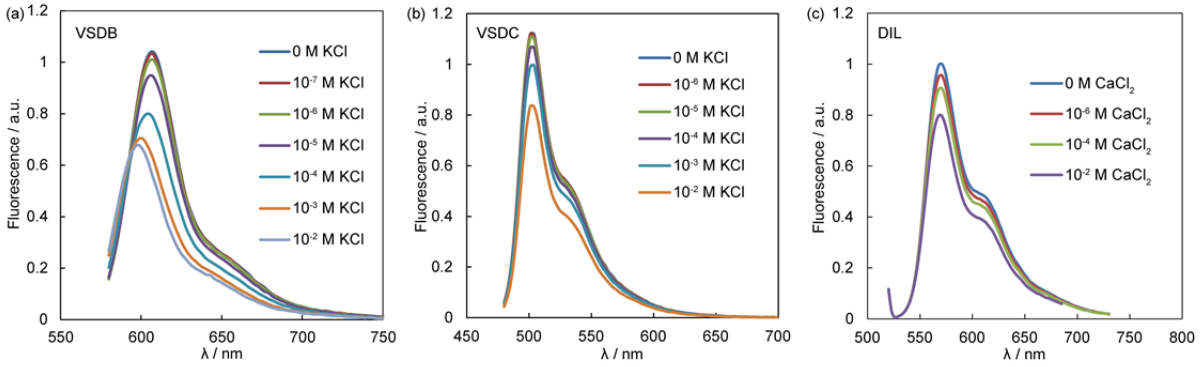

Figure S3. Emission spectra for K^+ selective nanospheres containing VSDB (a) and VSDC (b) and Ca^{2+} selective nanospheres containing DIL (c) to different KCl and $CaCl_2$ concentrations as indicated.

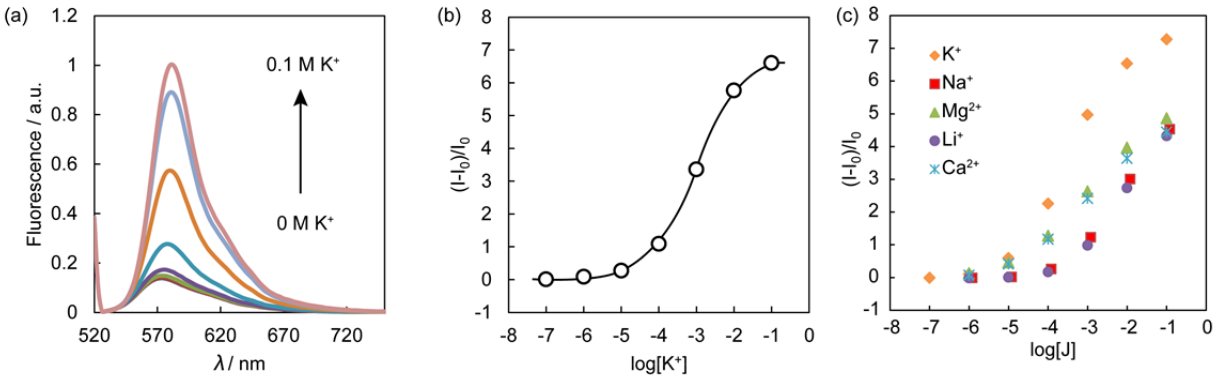

Figure S4. (a) Fluorescence spectra of M540 containing K^+-sensitive nanosphere suspension with increasing KCl concentration as indicated on the x-axis of Figure S4 b (white circles); excitation: 510 nm). (b) Corresponding calibration using emission intensity at 582 nm. $(I-I_0)/I_0$ represents the relative intensity change where I_0 is the emission intensity without addition of KCl. (c) Selectivity for the M540 containing K^+-sensitive nanospheres in H_2O. The counter ion for all salts is Cl^-.

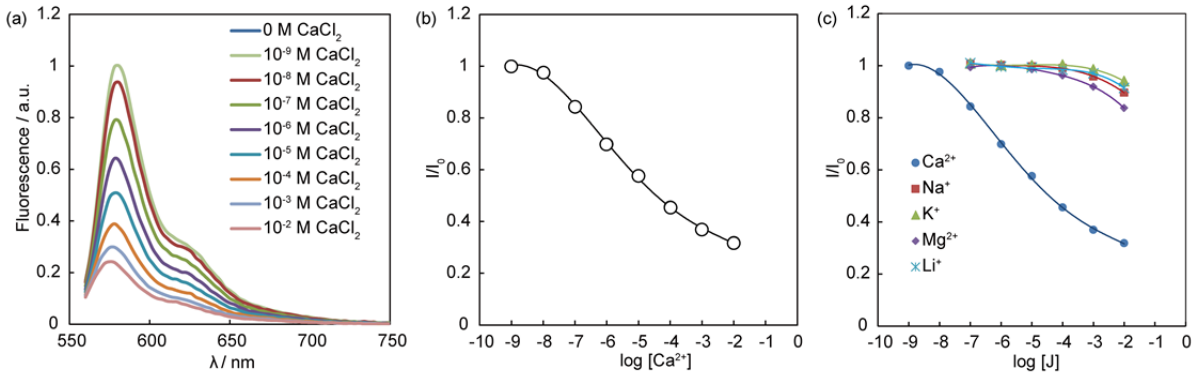

Figure S5. (a) Fluorescence spectra of VSDA containing Ca^{2+}-sensitive nanosphere suspension with increasing $CaCl_2$ concentration as indicated on the x-axis of Figure S4 b (white circles). (b) Corresponding calibration using emission intensity at 582 nm. I/I_0 represents the relative intensity change, where I_0 is the emission intensity without addition of $CaCl_2$. (c) Selectivity for the VSDA containing Ca^{2+}-sensitive nanospheres in H_2O. The counter ion for all salts is Cl^-.

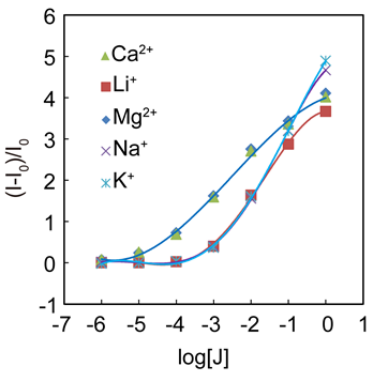

Figure S6. Ion selectivity of M540 containing Ca^{2+}-selective nanospheres without ionophore. Chloride was used as counter ion for all salts.